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Polarization Induced Pairing: an Excitonic Mechanism for High T_c

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The qualitative aspects of a recently proposed mechanism for superconductivity based on intra and interband Cu <-> O charge transfer excitations in the cuprates are reviewed. In this model, the dynamic polarizablility of the environment surrounding the CuO_2 planes plays an important role in enhancing T_c. The "sandwich" structures of $YBa_2Cu_3O_7$, $Bi_2Sr_2CaCu_2O_8$ and $Tl_2Ba_2Cu_3O_{10}$ are ideally suited to this mechanism. We briefly comment on the high T_c design principles suggested by the model.

The structural feature common to all the high temperature cuprate superconductors discovered to date[1] is the presence of two-dimensional sheets[2] of CuO_2. While much has been learned about th se materials in the past year, the pairing mechanism remains elusive. Current theoretical debate centers on the importance for the pairing interaction of the spin degrees of freedom vs. the charge degrees of freedom[3]. We have recently proposed a mechanism[4], the polarization induced pairing model, in which the planes are inherently susceptible to a superconducting instability due to the *emergence of low-lying charge transfer excitations when the system is doped* to a mixed-valence stoichiometry (i.e. Cu^{2+}/Cu^{3+}). These low energy charge fluctuations arise essentially because the electron affinity of Cu^{3+} is nearly equal to the ionization potential of O^{2-} in these materials; the configuration $Cu^{3+}O^{2-}$ is nearly degenerate with $Cu^{2+}O^{1-}$. In the same way that the polarizability of the lattice leads to an attractive interaction in conventional superconductors, the high electronic polarizability associated with this near degeneracy leads to an effective attractive interaction between electrons.

The theory evolved from an examination of *ab initio* configuration-interaction (CI) wave functions for a number of small clusters, as well as from a study of a semi-empirical two-band extended Hubbard Hamiltonian which incorporates the full periodicity of the lattice. The parameters which characterize the latter were chosen to be consistent with the *ab initio* results. For La_2CuO_4, both approaches predict the experimentally observed anti-ferromagnetic spin interaction when the now familiar Cu $d_{x^2-y^2}$ anti-bonding (AB) band is half-full (Cu^{2+}). As the system is doped away from half-filling, the magnetic interactions decrease in importance relative to a low-lying, finite wavevector($2k_f$), collective charge excitation within the Cu $d_{x^2-y^2}$ AB band. This collective charge excitation can be likened to a

charge-density wave without the static deformation of the nuclei, and is effective in mediating a Cooper pairing within the AB band. The expression for the critical temperature in weak coupling is analogous to that in conventional BCS theory,

$$T_c \sim \hbar\omega \; e^{-(1+\lambda)/(\lambda-\mu^*)} \qquad (1)$$

where the effective interaction between two electrons is given by $\lambda-\mu^*$, with λ the attractive component and μ^* the direct Coulomb repulsion, and $\hbar\omega$ is a characteristic energy[3]. Superconductivity requires a net attractive interaction, $\lambda > \mu^*$. Whereas the characteristic energy $\hbar\omega$ is of the order of the Debye temperature for conventional phonon-mediated superconductivity, it is of the order of a characteristic electronic excitation energy ("exciton") in the present mechanism, a feature contributing[5,6] to higher T_c.

While the model suggests that a single CuO_2 plane can support superconductivity, the critical temperature is greatly enhanced if the plane is embedded in a highly polarizable medium. In this regard, the "sandwich" structure[2] of $YBa_2Cu_3O_7$ and the newly discovered TlO and BiO compounds take on special interest. The beauty of the sandwich structures is that the "jelly" (the CuO_3 chains, or the BiO and TlO sheets) can not only enhance the intrinsic attractive interaction within a single plane (λ), but they also offer the possibility of mediating pairing between electrons in two distinct planes, thereby significantly reducing the direct Coulomb repulsion (μ^*).

In what follows, we focus on the manner in which we believe T_c is enhanced in the $YBa_2Cu_3O_7$ material. The details of the model are presented elsewhere[4]. Suffice it to say that it appears to be capable of rationalizing a great deal of the

existing experimental evidence. For example, the presence of two super-conducting phases in $YBa_2Cu_3O_{7-\delta}$, one around δ=0 (90K) and another around δ=.2-.3 (60K)[7]; the absence of an isotope effect[8]; the dependence of T_c on the Cu(2)-O(4) bond distance observed by Miceli et al.[9]; the independence of T_c to substitution of other rare earths for Y[10]; and the anisotropy of the gap function[11]. A number of new experimental directions[4] have been suggested which should shed some light on the validity of the model. However, it is our hope that the present communication will encourage the synthesis and characterization of new "sandwiches" with even higher T_c by enhancing the polarizability and coupling of the surrounding environment to the CuO_2 planes.

The structure of the 90K superconductor $YBa_2Cu_3O_7$ consists of two sheets of CuO_2 in the ab plane (the "bread"), separated by chains of CuO_3 which run along the b-axis[2](the "jelly"). The planes are weakly coupled to the chain in the c-direction by bridging oxygen atoms (O_4, Figure 1). What is the nature of the charge transfer which mediates the pairing? In addition to the collective charge excitation occuring in the planes, our calculations point to two excitations of importance involving the CuO_3 chain. The first involves the transfer of an electron from the non-bonding p_π band into the anti-bonding Cu $d_{y^2-z^2}$ band(Fig. 1). The transition dipole is directed perpendicular to the chain (the transverse exciton). *Ab initio* CI studies on the Cu_3O_{12} cluster shown in Fig. 1 suggest that the transverse excitation carries a large oscillator strength and requires an energy of the order of 0.1eV-0.5eV. This excitation favors intraplane pairing. In order to understand this qualitatively, imagine that an electron passes through the Cu in

the upper plane, and excites the charge transfer from O4 -> Cu1. The matrix element governing this process should be essentially Coulombic, i.e. W~1 / $r_{Cu2\text{-}O4}$. This creates a partial positive charge on O4 which can then attract another electron in the plane(Fig. 2a). The net enhancement[2] is given by

$$\lambda(\mathbf{k},\mathbf{k}') = -2n_c N_2(0)\, W^2 \int d\omega\, F(\mathbf{k},\mathbf{k}';\omega) \;/\; \omega \qquad (2)$$

where n_c is the density of chains, $N_2(0)$ is the density of states at the Fermi energy in the planes, and $F(\mathbf{k},\mathbf{k}';\omega)$ is essentially the wavevector and frequency dependent polarizability. Note that as the distance between the plane and O4 decreases, the coupling(W) between the conduction electrons and the charge transfer excitation increases. The model thus suggests that this distance should correlate with T_c. Note also that the orientation of the transition dipole for the transverse excitation is repulsive for interplane pairing.

The second important excitation involves Cu_1-O_1 charge transfer. In this case, the transition dipole is oriented along the chain (longitudinal exciton). Because of the extended nature of the chain, this is manifested as a collective excitation within the Cu $d_{y^2-z^2}$ band which can move down the chain with wavevector $2k_f$, where k_f is the Fermi wavevector. This precursor of a charge density wave is not necessarily commensurate with the lattice, but it can be pictured qualitatively as in Fig. 2b. It is strictly analogous to the collective excitation discussed earlier for a single plane, but because of the perfect Fermi nesting associated with one-dimensional systems[12], is even more effective in mediating Cooper pairing.

While the transverse exciton favors intraplane pairing, the longitudinal excitation has the proper symmetry to mediate both inter- and intraplane pairing. These two excitations enter into the expression for λ additively, so that the net attraction is greater for intraplane as opposed to interplane pairing. We suspect,

however, that the reduced direct Coulomb repulsion associated with interplane pairing will dominate, and that it is responsible[13] for the 90K transition in $YBa_2Cu_3O_7$. As oxygen is removed, the vacancies disrupt the chains, and the effectiveness of the longitudinal excitation decreases. At some point, presumably near $YBa_2Cu_3O_{6.7}$, the more localized transverse excitation becomes the dominant mode and we associate it with intra-plane pairing and the 60K plateau. As further oxygen is removed, the magnetic interactions become more important. At $YBa_2Cu_3O_{6.5}$, we reach a formal Cu^{2+} valence(the 1/2-filled band), and the Cu^{3+} character necessary for the low-lying charge transfer excitation vanishes.

If this model proves to be correct, it suggests that other high T_c materials should have the following design. The "bread" should be a good conductor (metallic) with a large density of states at the Fermi energy. It should be obvious that CuO plays no special role in the theory, except for the important feature that the electron affinity of Cu^{3+} is similar to the ionization potential of O^{2-} in this lattice, thereby paving the way for the low-energy charge transfer modes[14]. In this sense, likely candidates could be selected based upon their proximity to a CDW instability. The plane should be weakly coupled to a highly polarizable medium. The latter might be either one- or two-dimensional, but the perfect nesting features at any band-filling associated with chains lead to a particularly enhanced polarizability at $2k_f^c$. The maximum attraction λ is achieved when the Fermi wavevector in the chain is similar to that in the plane, since the formation of a Cooper pair in the plane $(k_f^p,-k_f^p)$ requires a momentum exchange $2k_f^p$, which is precisely what is available in the collective excitation in the chain if $k_f^c=k_f^p$. In order to maximize the coupling to this excitation, the bridging ligands should be as close to the planes as possible and weakly interacting. The latter is ensured in

$YBa_2Cu_3O_7$ by having the conduction band composed of $d_{x^2-y^2}$ character, which is orthogonal to the bridging $O(p_z)$ orbital. If this were not the case, the system might be expected take on three-dimensional metallic behavior and the benefits associated with the reduced dimensionality and the separation between the conduction electrons and the polarizable medium would be lost. In order to minimize the direct repulsion μ^*, the planes should be as far apart as possible. There will be, however, some optimal separation where the reduction in the Coulomb repulsion is balanced against the loss in the interplane pairing interaction. It is, of course, easier to stipulate these criteria than it is to realize them, but there seems to be no *a priori* reason they could not be artificially designed and synthesized in other materials.

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13. Another possibility for the two critical temperatures involves intraplane pairing only. The effectiveness of the longitudinal excitation is maximized with

well-ordered chains, i.e. $YBa_2Cu_3O_7$. In the 90K phase, both the longitudinal and transverse excitations contribute to intra-plane pairing. Near $YBa_2Cu_3O_{6.7}$, the oxygen vacancies have disrupted the chain, and only the transverse excitation remains to enhance T_c.

14. The extended Hubbard model discussed in reference 4 exhibits a superconducting instability when ϵ_d-$\epsilon_p \leq t_{pd}$ and $V > U/4$, where ϵ_d, ϵ_p are the bare site energies for a Cu3d, O2p electron, t_{pd} is the hopping integral, and V and U are nearest-neighbor and on-site Coulomb repulsions projected onto the AB band. These quantities are defined more precisely in reference 4.

Figure captions:

Figure 1) A Cu_3O_{12} cluster model of the sandwich structure of $YBa_2Cu_3O_7$ is shown on the left. It consists of three Cu atoms and their nearest-neighbor oxygens. The upper and lower Cu(2) have the coordination of the planes, while the central Cu(1) is an element of the chain which runs along the b-axis. Two important bond distances are labeled r_1 and r_2. To the right of the cluster are shown the three molecular orbitals which evolve from the $d_y2_{-z}2$ orbital on Cu(1) and the p_z atomic orbitals on the two O(4) sites. They are classified by the number of nodes as bonding(B), non-bonding(NB), and anti-bonding(AB), and contribute to the B,NB, and AB bands of the chain shown below. The phase of the orbitals is denoted by color; the $d_x2_{-y}2$ orbitals in the planes are shown for the reader's orientation. In the limit that the chain was purely Cu^{3+}, the B and NB bands would be full, and the AB band empty. The transverse excitation described in the text corresponds to an interband transition in which an electron is transferred from NB ->AB.

Figure 2a) A schematic of the way in which the transverse excitation enhances the intra-plane pairing. Excitation of an electron from the NB band to the AB band(Fig.1) results in charge transfer from the bridging oxygen to the central Cu. This leads to a partial positive charge on O(4) which can mediate intra-plane pairing. The enhancement is dependent on the Cu(2)-O(4) distance as well as the energy and oscillator strength of the transition.

2b) A schematic of the collective excitation within the anti-bonding band, the longitudinal exciton. This excitation has the proper symmetry to mediate both inter- and intraplane pairing.

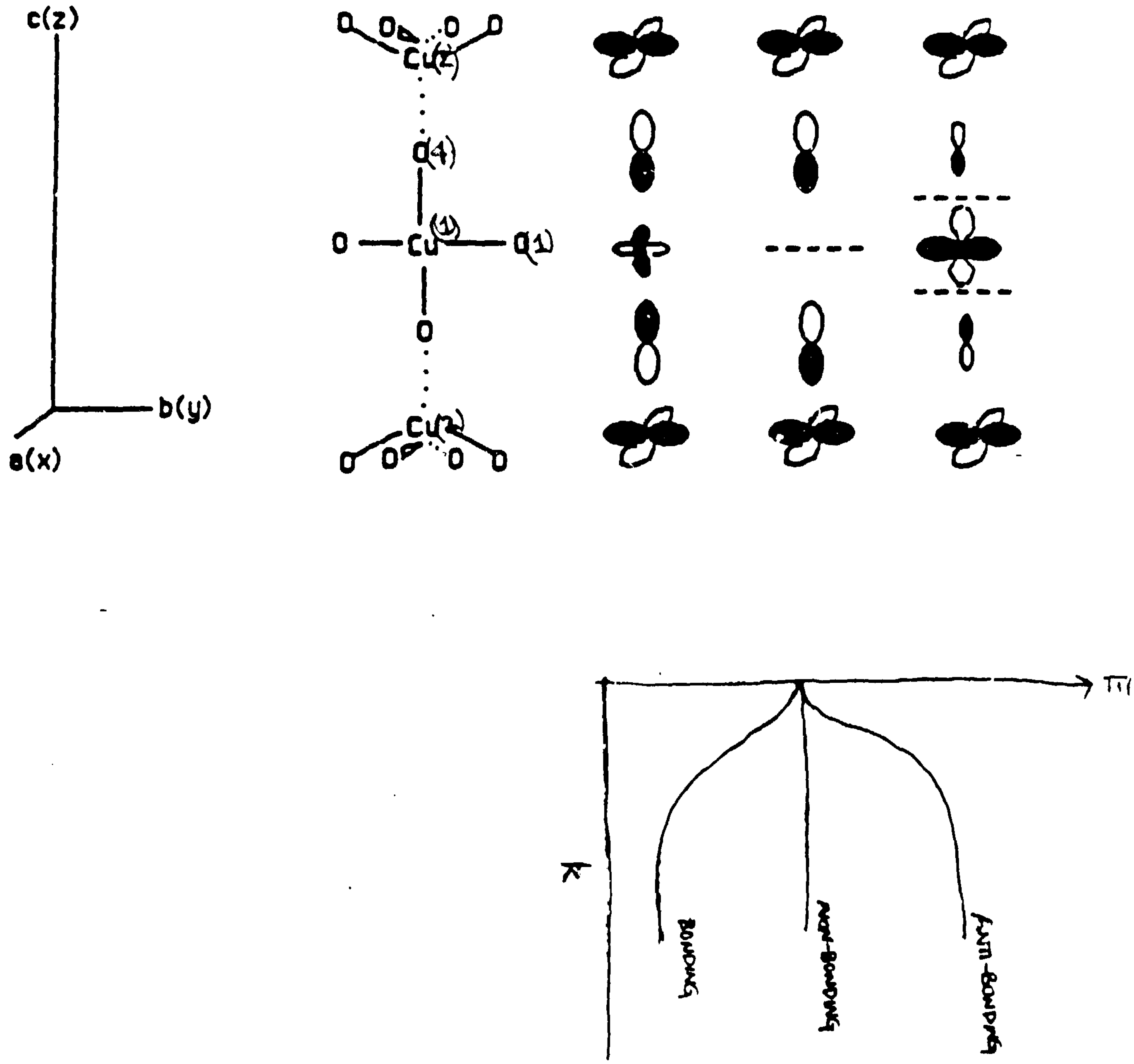

FIGURE 1.

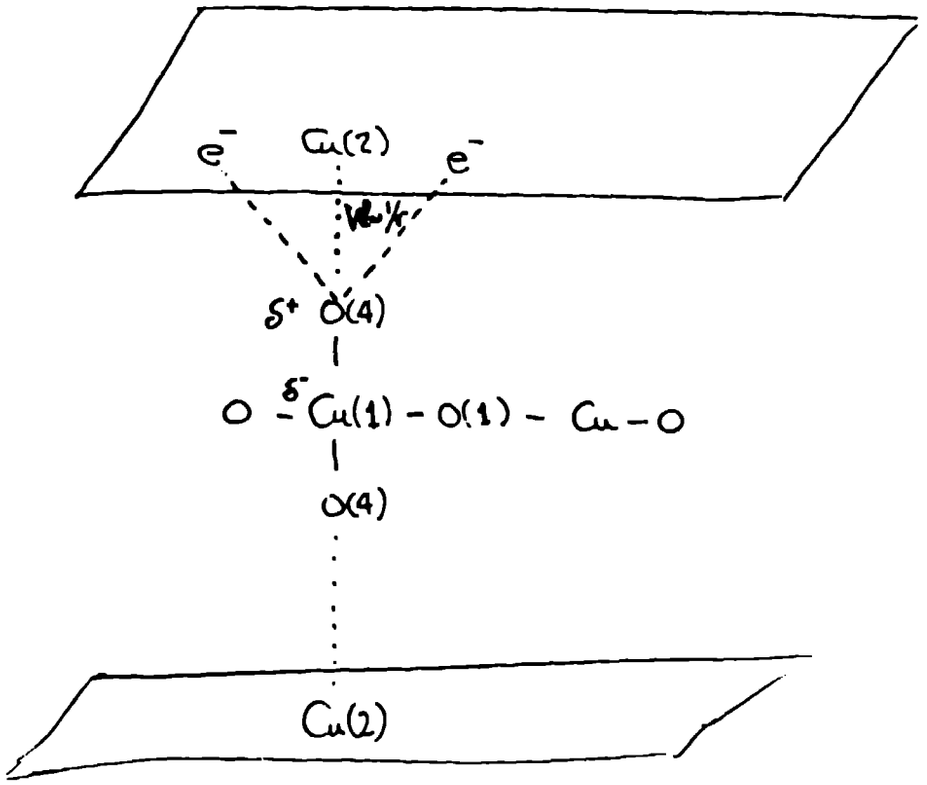

Figure 2a)

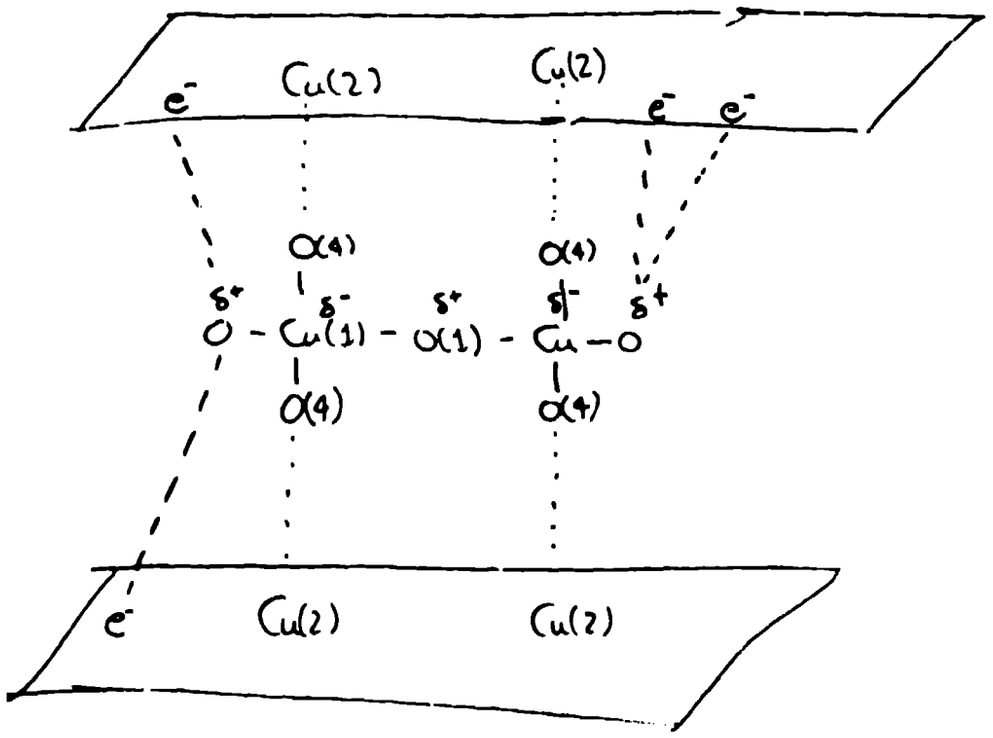

Figure 2b)